TECHNICAL DIVISION
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AMMONIUM NITRATE IN THE VESSEL VENT SYSTEM

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DISCLAIMER

INTRODUCTION

During the past several years amounts of ammonium nitrate (AN) ranging up to several thousand kilograms (usually in solution) have been found in the vessel vent filters of both canyon buildings. Recently, difficulties were encountered with the development of high pressure drops across the filter in the H-Area hot canyon that led to the discovery of 600 kg of dry AN. Problems with increased pressure drops subsequent to the replacement of this filter led to the conclusion that AN was again accumulating in the filter. SRL was asked to evaluate the hazard of these AN accumulations, help determine the source of ammonium ion that produced them, and to suggest methods for preventing them. This report summarizes the SRL studies in response to this request, and also contains background information on the ventilation system serving the vessel vent filters, the filters themselves, and the history of ammonium nitrate accumulations.

Little information is available on the behavior of ammonia in canyon processing. The hazards of ammonium nitrate in the separations process were first investigated by Mobley[1] who examined the fate of small ($<$50kg) amounts of AN in waste evaporation. In conjunction with the current studies analysis was made of the structural damage anticipated from the hypothesized detonation of 600kg of ammonium nitrate in a canyon.[2] Other recent studies and observations relating to accumulation of ammonium nitrate are cited elsewhere in this paper.

SUMMARY AND CONCLUSIONS

The quantities of ammonium nitrate that have accumulated periodically in the F and H canyon process vessel vent filters are large enough to produce pressurization and serious damage to the canyon if they were to explode. However, only one credible mechanism for initiating an explosion has been identified: a large canyon fire that would feed hot air from several sections of the canyon into the process vessel vent system. In this case it is not certain that an explosion would occur, but a hazard of such explosion would exist.

Accumulation of ammonium nitrate in the filters can be reduced by flushing the filters or by eliminating ammonia-producing reactions. Accumulation of ammonium nitrate could be eliminated by destroying ammonium ion prior to neutralization, by reacting ammonium ion to prevent its volatilization, or by destroying ammonia in the gas phase. The two measures for reducing accumulations have been implemented in the Plant. Of the methods for eliminating ammonia althogether, reaction with nitrous acid in solutions during or after waste evaporation and prior to neutralization appears most practical and easiest to implement.

DESCRIPTION OF VESSEL VENT SYSTEM

Process Vessel Vent System [3,4,5]

All canyon vessels except the section 6H dissolvers and their associated off-gas reactors and filters are connected to the process vessel vent system.

The vessels are maintained at a slight vacuum with respect to the canyons by two exhausters located in each of the 292-1 buildings. These 50 HP units are rated at 5830 cfm in H-Area and 4800 cfm in F-Area. Canyon air flows into the vessels through their overflow lines and exits into the vessel vent header.

The canyon vessels connect to 18-inch vent headers (vessel vent headers) encased in concrete located along the outside walls of the respective air exhaust tunnels. The canyon waste headers and the gravity drain headers are also ventilated by these vent headers. At section 5 of the warm canyons and section 7 of the hot canyons, the vent headers enter the canyons: where the air passes through dehumidifiers 5.6H or 7.3H and filters 5.7F or 7.2F to remove radioactive particulate matter. In H-Area a scrubber has been substituted for the dehumidifier at 7.3H (hot canyon). After the air is filtered, it returns to the vent headers located in the canyon air exhaust tunnels. The vent headers from the hot and warm canyons form a common header in the canyon air exhaust tunnel.

The common vent header leads to the exhausters at the 292-1 buildings. Air from the fans is exhausted to the canyon air exhaust tunnel ahead of the sand filters. Both exhausters are on the building 292 emergency power system. Normally only one exhauster is in operation; the second is held in standby. The normal flow through each branch of the system (hot canyon and warm canyon branch) will be no greater than half the rated capacity of one of the fans or 2915 cfm in H-Area and 2400 cfm in F-Area. It has been estimated that the average flow through a single tank into the vessel vent header is about 60 cfm.

The process vessel vent exhausters normally maintain a vacuum at the fan of 21 inches of water in H-Area and 25 inches of water in F-Area. If the vacuum drops to less than 18 inches of water in H-Area or 16 inches of water in F-Area the standby exhauster starts and an alarm sounds.

In the Building 221 gang valve corridors, pressure taps extend through the floor and connect to the vent header at Section 5 (warm canyon) and Section 7 (hot canyon). They are used for sampling and measuring the vacuum in the vessel vent header.

Dehumidifiers

A dehumidifier is located near the south end of each canyon, and is installed in series with the process vent header. In the original installation, excess moisture was condensed from process gases by cooling and the chilled gases were reheated before leaving the dehumidifier to avoid wetting the "Fiberglas" filter. The dehumidifiers are no longer operated because of leaks in heating and cooling coils, and humid air enters the process vessel vent filters. The exception is H-Area hot canyon where a scrubber has replaced the dehumidifiers.

The construction of the dehumidifiers is as follows. A 12-inch diameter inlet at the bottom of each dehumidifier connects with the process vessel vent header at the point where it comes through the canyon wall into the canyon from the exhaust air tunnel. The cooling section of the dehumidifier takes up approximately the lower two-thirds of each unit and is filled with coils of 3/4-inch OD, 16-gauge stainless steel tubes totalling 540 square feet of cooling surface. Above the cooling coils are two horizontal perforated plates, 1 inch apart, through which cooled gases pass into the heating section. The plates function as a thermal barrier between the cooling and heating sections. The heating sections, made of 3/4 inch OD, 16 gauge stainless steel are located in the top third of each dehumidifier and have a total of 51 square feet of coil surface. A 12-inch diameter outlet is located at the top of the dehumidifiers carries the gases to the vessel vent filter. A drain outlet at the bottom draws off condensate by gravity to a condensate tank.

In the H-Area hot canyon the dehumidifier is replaced by a scrubber in which the gases pass through a packed tower where they can be washed with caustic, water, or other solutions. This scrubber was once throught to be useful for removing iodine from the gases when short-cooled materials were being processed, but it is not used for that function any longer.

Vessel Vent Filter

The vessel vent gas filter (Figure 1) is contained in a canyon vessel that is 8 feet in diameter and 15 feet 7 inches high. The inside of the vessel is divided and sealed into two separate sections, upper and lower, each approximately 7 feet 9 inches high. The packing depth of the filter material in each Section is 4 feet 7 inches; the packing is located about equally distant from the top and bottom of a section. Each filter is packed with layers of "Fiberglas" of varying densities and each layer is supported on frames of 4-mesh stainless steel screen. The inlet side of each filter is at the bottom. Beginning with the bottom layer the following list describes the sequence, density and depth of the "Fiberglas" layers.
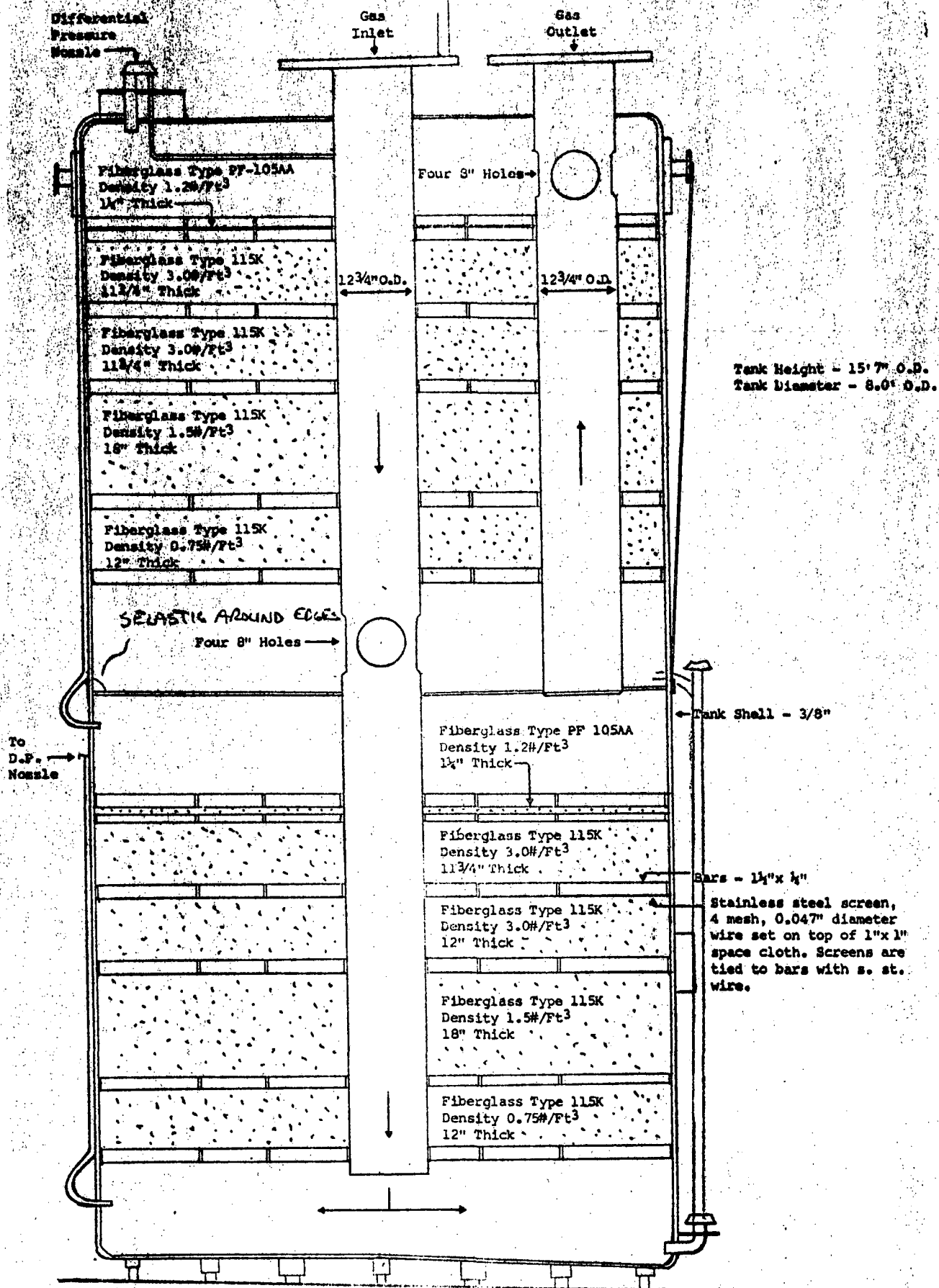
Vent Gas Filter Packing

Layer	Density, lb/ft^3	Depth, inch
1	0.75	12
2	1.5	18
3	3.0	12
4	3.0	11-3/4
5	1.2	1-1/4

The 12-inch inlet and outlet nozzles are located on the top of the vessel. The 12-inch inlet pipe is open at the lower end and extends down the center of the vessel to a point below the first filter layer in the lower section. Four equally spaced 8-inch holes are cut in the inlet pipe at the level of the inlet space beneath the first layer of the upper filter and above the divider plate that seals the two sections from each other. The 12-inch outlet pipe is open at the lower end and extends through the upper filter section to a point just below the divider plate. Four equally spaced 8-inch holes in the pipe exhaust the air above the top layer of the upper filter. This arrangement permits

Figure 1

PRO...

Differential Pressure Nozzle

Gas Inlet

Gas Outlet

Fiberglass Type PF-105AA
Density 1.2#/Ft³
1¼" Thick

Four 3" Holes →

Fiberglass Type 115K
Density 3.0#/Ft³
11¾" Thick

12¾"O.D.

12¾" O.D.

Fiberglass Type 115K
Density 3.0#/Ft³
11¾" Thick

Fiberglass Type 115K
Density 1.5#/Ft³
18" Thick

Fiberglass Type 115K
Density 0.75#/Ft³
12" Thick

SELASTIC AROUND EDGES
Four 8" Holes →

To
D.P. →
Nozzle

Fiberglass Type PF 105AA
Density 1.2#/Ft³
1¼" Thick

Fiberglass Type 115K
Density 3.0#/Ft³
11¾" Thick

Fiberglass Type 115K
Density 3.0#/Ft³
12" Thick

Fiberglass Type 115K
Density 1.5#/Ft³
18" Thick

Fiberglass Type 115K
Density 0.75#/Ft³
12" Thick

Tank Height - 15'7" O.D.
Tank Diameter - 8.0' O.D.

← Tank Shell - 3/8"

Bars - 1½"x ¼"

Stainless steel screen,
4 mesh, 0.047" diameter
wire set on top of 1"x 1"
space cloth. Screens are
tied to bars with s. st.
wire.

equal flow of gas through both filter sections. The exit streams are combined before they enter the outlet header, which connects with the process vent header at a point where it goes back through the canyon wall between the canyon and the exhaust air tunnel.

In April of 1974 the filter in the H-Area hot canyon was replaced by a new high efficiency filter because of releases of alpha-emitting radionuclides to the stack. This filter is similar to the older version but has baffles to prevent the gas from bypassing the filter and a tap in the bottom to permit detection and draining of liquid that might accumulate there.

<div align="center">

HISTORY OF AMMONIUM NITRATE ACCUMULATIONS[6]

</div>

H-Area Hot Canyon

In March of 1974 H-Area experienced releases of alpha emitting nuclides to the stack. Consequently, in April the vessel vent filter was replaced with the new high efficiency filter. While removing the old filter, 3.5 ft of liquid was found in its bottom section. The liquid was shown to contain ammonia but no quantitative analysis was made.

During the three-month period preceding July 25, 1975, the pressure drop across the new filter increased markedly and on that date it plugged completely. The canyon building was shut down on July 28 for a 12-day period while the filter was flushed with water and replaced. No liquid was found in the bottom of the filter but the flushes contained 600 kg of ammonium nitrate. About 117 kg of ammonium nitrate was also found in the vessel vent scrubber at this time.

The vessel vent system was placed back in service on August 9, 1975 and initially operated well. In September, however, pressure drop (ΔP) increases were again observed; by October ΔP had increased to 8.9" of water (startup ΔP was about 6.0" of water). The increases were found by Works Technical to occur primarily during neutralization of concentrated frame waste raffinate. Sixty kg of additional ammonium nitrate was found in the vessel vent scrubber during September.

The ammonium nitrate in the H-Area hot canyon filter was solid; that in the other canyon filters (described below) was in solution. This is because only the air entering the H-Area hot canyon filter was heated to about 80°C by steam coils in the vessel vent scrubber. (This temperature is now restricted to 50°C.) Ammonium nitrate is very hygroscopic and will go into solution any time the partial pressure of water in air rises above the vapor pressure of its saturated solution. (Approximately 60% relative humidity at 30°C.)

H-Area Warm Canyon

In January 1973 large pressure drops were observed across the vessel vent filter so that the canyon had to be shut down. Twenty-nine thousand pounds of liquid, composed of 6.7M-7.8M ammonium nitrate, was removed. The filter was estimated to have contained 5800 kg of ammonium nitrate.

In August 1975 the warm canyon vessel vent filter was inspected while the canyon was shut down to replace the hot canyon filter. Six to seven feet of liquid was found that sealed off the lower half of the filter. Ammonium nitrate (4380 kg was estimated to be in this liquid.) An additional 50 kg of AN was found associated with the dehumidifier condensate. The filter was returned to service without flushing.

F-Area Hot Canyon

In April 1974 the canyon was shut down after the inlet pressure to the vessel vent filter decreased from 5-8 inches of water to 1 inch over a period of months. The filter was found to contain 12900 liters of liquid containing ammonium nitrate at a NH_3 concentration as 3.8 grams/liters. The filter was estimated from analyses of the liquid and flushes to contain 250 kg ammonium nitrate.

F-Area Warm Canyon

The warm canyon vessel vent filter was examined in April of 1974 when the hot canyon was shut down to inspect its filter. The filter contained 9,900 liters of liquid containing 1.9 grams NH_3/liter. Analyses of the liquid and flushes showed the filter had contained about 100 kg ammonium nitrate.

<div align="center">HAZARD EVALUATION</div>

Reactions of Ammonium Nitrate

Ammonium nitrate (AN) has been used for over fifty years in explosives and as an agricultural fertilizer and in general has been considered relatively safe. However, a number of very serious fires and explosions have given rise to investigations of the hazards of ammonium nitrate. [7-11]

The hazard of AN arises from its exothermic decomposition to produce gaseous products, leading under certain circumstances to an explosion. This reaction of AN is influenced by the acidity, the presence of catalysts such as dichromate or chloride, and the presence of organic material such as wax or paper.

Chemically pure AN decomposes above the melting point (169°C) as follows:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad \Delta H_{25°C} = -8.8 \text{ KCal/mole}$$

Other reactions produce other oxides of nitrogen, NO_2 and NO. The decomposition reaction producing the greatest volume of gas per mole of AN is:

$$NH_4NO_3 \rightarrow N_2 + 1/2 \; O_2 + 2 \; H_2O \qquad \Delta H_{25°C} = -27.7 \text{ KCal/mole}$$
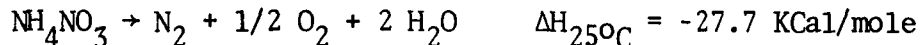
If organic matter is present, considerably more energy is evolved:

$$NH_4NO_3 + 1/3 \; CH_2 \rightarrow N_2 + 1/3 \; CO_2 + 7/3 \; H_2O \qquad \Delta H_{25°C} = -77.3 \text{ KCal/mole}$$
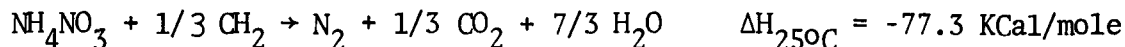
Here CH_2 represents a hydrocarbon with an atom ratio of 2 hydrogens to one carbon. The exact amount of heat released will of course depend on the exact nature of the organic material involved and the products formed.

Kinetics

Most of the early work on the rate of thermal decomposition of AN has been summarized in references 9 and 10. A diagram (extracted from reference 9) showing the rates of decomposition as a function of temperature for AN containing catalysts and other additives is given in Figure 2. The reaction is generally first order but an induction period frequently preceeds the more rapid decomposition. The reaction rate is slowest for chemically pure AN (CPAN), more rapid for fertilizer grade ammonium nitrate (FGAN), which is coated with wax; and still more rapid if the FGAN is mixed with paper. The decomposition of CPAN is catalyzed by chloride ion, nitric acid, or heavy metal salts, particularly chromates or dichromates. The catalysts are effective at lower temperatures; above about 300°C the rates are about the same as with CPAN, although the decomposition products may be different.

More recent kinetic studies [12-17] have been aimed at establishing the mechanism of the reactions. Some of these studies have also shown the importance of the composition of the vapor phase on the reaction rate; both water and ammonia in the vapor retard the reaction, while nitric acid accelerates it. This explains many of the erratic results obtained previously.

In subsequent safety analyses the following equation will be assumed to describe the decomposition rate of AN in the vessel vent system.

$$K(sec^{-1}) = 4.4 \times 10^{9} e^{-\frac{15000}{T}} \tag{1}$$

$$or \quad lnK = 22.200 - \frac{15000}{T}$$

Where K is the specific rate constant in sec^{-1} and T is the temperature in °K. This equation corresponds roughly to a line drawn through the points for dichromate catalyzed AN and for FGAN + paper in Figure 2. These are the largest rate constants found except for those due to chloride catalysis, which are not applicable to the chloride-free SRP system.

The decomposition of CPAN as shown in Figure 2 can be expressed by:

$$K = 8.8 \times 10^{19} e^{-\frac{29300}{T}} , or \tag{2}$$

$$lnK = 45.924 - \frac{29300}{T}$$

These equations are also applicable to the decomposition of all AN samples above about 300°C.

MODES OF THERMAL DECOMPOSITION

Fume-Off

If ammonium nitrate is heated to about 250°C, where its decomposition proceeds at an appreciable rate, and is then insulated its temperature will continue to rise at an increasing rate; the heat generated by the reaction will increase the temperature which in turn will increase the rate of reaction and

Figure 2
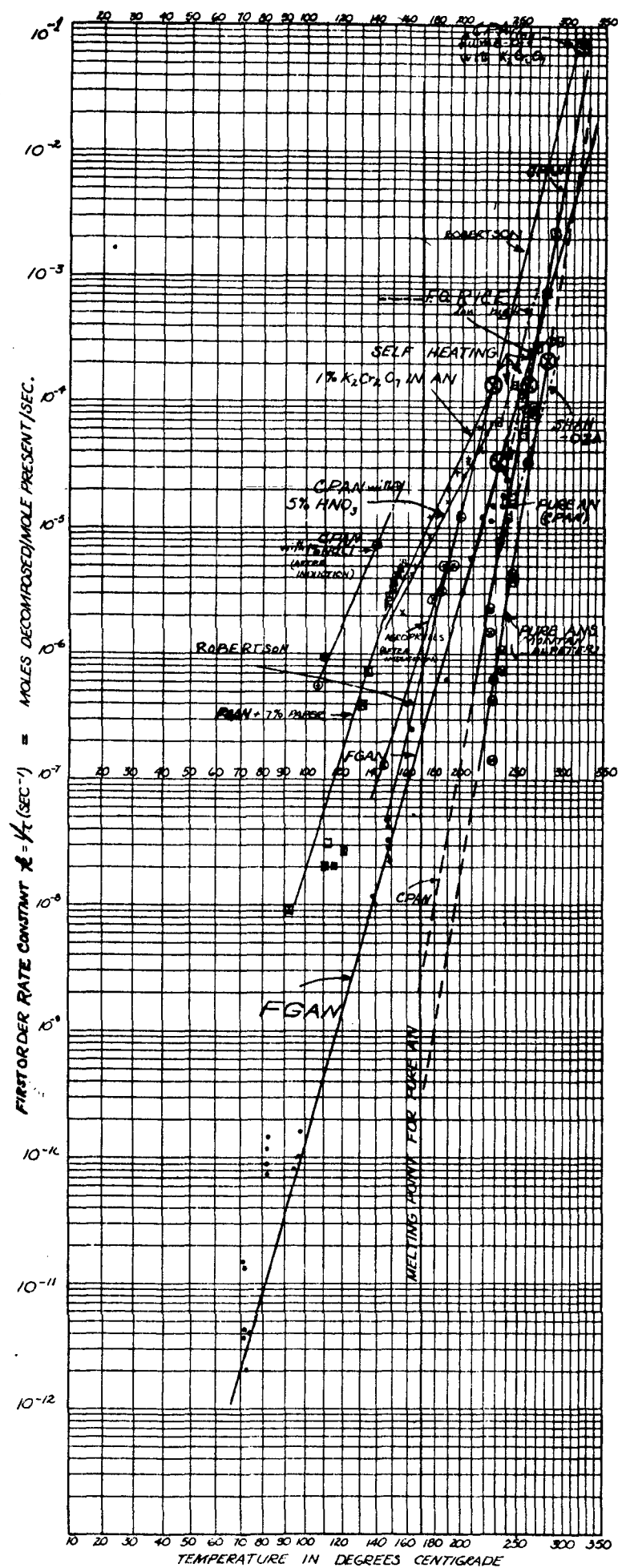
FIGURE-1

Arthur D. Little, Inc.

hence heat generation. If no other process intervened, an explosion would inevitably result. In practice, however, the temperature in such a system rises to about 290°C at atmospheric pressure and remains constant until all ammonium nitrate is consumed.

The explanation of the this temperature-limiting process was found by Feick and Hainer. [18] Two processes are involved, the irreversible decomposition

$$NH_4NO_3(1) \rightarrow N_2O(g) + 2 H_2O(g)$$
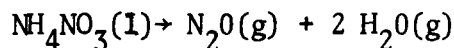
and the reversible dissociation

$$NH_4NO_3(1) \rightarrow NH_3(g) + HNO_3(g)$$

The first reaction is exothermic but the second is endothermic. As the temperature increases the reversible dissociation pressure increases with temperatures according to the equation:

$$\log_{10} p \text{ (cm of Hg)} = -4109/T + 8.502 \tag{3}$$

The gases generated by the first reaction become increasingly saturated with NH_4 and HNO_3 as the temperature rises and therefore, remove a larger amount of heat, because they carry away larger amounts of dissociation products. When the heat generated by the exothermic decomposition is just equal to that absorbed by the reversible dissociation, the temperature remains constant. Fume-off reactions generate copious quantities of smoke caused by the condensation of NH_3 and HNO_3 into NH_4NO_3 when the gas cools.

Feick and Hainer derived a relation between the equilibrium pressure p of the dissociation process and the total applied pressure P

$$P = \left[1 + \frac{3}{2} \left(\frac{\Delta Hv}{Q - \Delta Hr} \right) \right] p \tag{4}$$

Where ΔHv is the enthalpy change of the reversible dissociation reaction, ΔHr is the enthalpy change of the irreversible decomposition, and Q is heat added to the system for external source (Q is 0 from an adiabatic process).

It is apparent from this equation that if the applied pressure P is increased, the vapor pressure, p, will increase and the temperature of the ammonium nitrate must increase as well because p is a monotonically increasing function of temperature. AN will, therefore, often explode if heated in a confined space. The pressure buildup due to escaping gas will cause the temperature to rise and ultimately lead to a run-away reaction. Studies by J. J. Burns (Ref. 8, page 16) shown that FGAN containing 1.5% paper will explode if the pressure exceeds 250 psi while pressures in excess of 2000 psi are necessary for CPAN to explode. The difference is probably caused by the larger heat of reaction of the FGAN.

Propellant Burning

If the surface of solid AN is heated intensely, a thin layer may melt and begin decomposing. Some of the gases evolved, N_2O, NH_3 and HNO_3, may

then undergo further reaction in the vapor phase to produce a flame. Some of the heat generated in the gas phase may heat the solid causing further melting and decomposition thus leading to a self sustained surface fire called propellant-type burning. This type of burning is not thought to be likely to accelerate rapidly even if improperly vented because only a small amount of AN is involved at a time (reference 9, Page II-47).

Fume-Off Burning

If liquid ammonium nitrate is already undergoing a fume-off reaction the product gases, N_2O, NH_3 and HNO_3 can react in the gas phase. The principal effect is to increase the heat generated over that obtained from a simple fume-off reaction, and thus to increase the danger of an explosion if venting is inadequate.

Explosions

The term explosion is generally applied to any very rapid chemical reaction that generate gaseous products. Two types of explosions are re-cognized in the explosive trade: deflagrations and detonations.

Deflagration describes a rapid burning process which spreads through-out a material by mass flow and heat flow. The process is relatively slow with burning rates of the order of centimeters per second for propellants. For gun powder (where impulse is desired rather than shock) the burning rate is about 500 cm sec^{-1} in air at atmospheric pressure. A thermal explosion of a moderate amount of ammonium nitrate in a confined space would probably be classified as a deflagration. Heating AN to 400°C and 460°C would lead to nearly complete fume-off in 3 and 0.03 seconds respectively; these rates are fairly slow as explosions go.

Detonation describes the rapid burning process initiated by a shock wave traveling at greater than the velocity of sound. AN has an ideal detonation velocity of 300,000 cm sec^{-1} but measurements on practical size charges range from 150,000 to 250,000 cm sec^{-1}. Detonations in AN nitrate can be initiated by another explosive such as dynamite. Frequently in large amounts of ammonium nitrate a deflagration can generage a detonation; the conditions required for this to happen are not well understood.

F. A. Loving has studied the sensitivity of AN[19] and determined that although there have been a number of bad explosions and fires with pure AN, such events are much more likely to occur with impure material. Organic matter not only sensitizes the decomposition but also reacts with oxygen produced in the decomposition to increase the energy released. Cellulosic materials and dust are particularly bad. Fires have occurred when AN and dust have accumulated on steam pipes. Other materials that sensitize AN include sulfur, sulfides, chloride, and Zn and Mg dust. Hydrazine and hydroxylamine nitrates may sensitize AN since they are similar in composition to methyl ammonium nitrate, a sensitizer.

AN that contains impurities is not stable at 225°F (107°C) or higher for prolonged periods (e.g. 48 hours). It will eventually undergo rapid decom-position. Material in our vessel vent filter is probably safe because it does not exceed 50°C. The heating of our filter by fires or self-heating during a prolonged shutdown is considered later in this report.

Mechanisms for Exploding AN in the Vessel Vent System

Explosions are usually generated either by impact or by fires or other exothermic reactions.

Impact

Ammonium nitrate is not very sensitive to impact. A shock wave of 30 kilobars is required to initiate a detonation, and thus a rifle bullet fired into a charge will not set it off.[19] Boostering of AN by dynamite is required to cause an explosion. It is therefore, unlikely that any impact occurring in the canyon building (such as dropping a cell cover, etc.) could ever cause AN to explode.

Fires or Exothermic Reactions

A fire or fume-off reaction in ammonium nitrate can turn into an explosion. There is no way of predicting exactly under what circumstances such events will occur. Certain crude generalizations, however, can be made: (1) explosions are more likely to result with large amount of ammonium nitrate than with small amounts, and (2) they are more likely to occur in confined places than in unconfined one. F. A. Loving[19] gave the following subjective view of the magnitude of the hazard as follows: He said that he would not hesitate to fight a fire involving 100 pounds of AN; he would be concerned about fighting one involving 1000 pounds, he would never fight a fire involving a boxcar load of AN, but would evacuate the area.

In view of the high sensitivity of AN containing impurities and the fact that impurities are probably present in the vessel vent filter it seems likely that a fire involving 1000 pounds or more of AN might turn into an explosion. The fact that the material in the filter is confined would also increase this probability. In the following discussions it will be assumed that any fire or fume-off will lead to an explosion and the hazard is related to the probability of these events. The only cause of fire or fume-off that have been identified are either an external fire in the canyon buildings, or self-heating of the AN. The following discussions on fires and self-heating will apply to dry AN as in the H-Area hot canyon filter. The other filters, in which AN is in solution, will be somewhat safer because the water must be evaporated before it can heat to a dangerous temperature.

Self-Heating

The decomposition of AN proceeds at a finite rate even at room temperature. If no heat is removed, the temperature will increase at an ever-increasing rate until a dangerous reaction ensues. Conditions necessary for such self-heating to occur in the vessel vent filter are calculated in this section for normal operating conditions and for the case where ventilation is shut off and heat must be transferred by conduction alone to the walls of the filter. The rate at which the filter would heat up if the system was completely insulated is also calculated.

Normal Operating Conditions

Under normal operating conditions air passes through the filter at about 2900 cfm. As it traverses the filter it picks up heat from the decomposing AN and removes it from the filter. The question we wish to answer is: under what conditions of initial temperature and flow will all of the heat generated by AN decomposition be removed by the air.

In the following discussion the AN will be assumed to be uniformly distributed throughout the filter and at thermal equilibrium with air. The heat transfer from the AN to the air should be rapid because of its small particle size.

Consider an element of length dx of the filter containing dn moles of AN, through which air is flowing in a positive direction with a mass flow of W grams per second. Heat balance about the incremental length gives at steady state

$$Q_g = W C_p dT \qquad (5)$$

Where Q_g is the heat generated per unit time within dx and dT is the temperature change across it, C_p is the heat capacity of air at constant pressure.

The heat generated within the increment is given by

$$Q_g = dn \ (-\Delta H) \ A \ e^{-B/T} \qquad (6)$$

Where $(-\Delta H)$ is the negative enthalpy of the decomposition reaction, A and B are parameters of the Arrhenius equation, and T is the temperature in $^\circ K$.

However, since the AN is uniformly distributed

$$dn = \frac{n}{\ell} dx \qquad (7)$$

where n is the total number of moles of AN in the filter and ℓ is its length.

n can be written in terms of the total number of kilograms M of ammonium nitrate within the filter

$$n = \frac{1000M}{80} \qquad (8)$$

(80 is the formula weight of AN)

Combining the above equations

$$\frac{dT}{dx} = \frac{1000}{80} \frac{(-\Delta H)}{W} \frac{AMe^{-B/T}}{C_p \ \ell}$$

The above equation can be integrated but the form of the solution is not convenient to use. The following approximation is therefore made.

$$\frac{B}{T} = \frac{B}{T_i} \ \frac{1}{(1 + \frac{T-Ti}{Ti})} \ \approx \ \frac{B}{T_i} \ (1 - \frac{T-Ti}{Ti}) \qquad (10)$$

Where T_i is the initial air temperature, if we define

$$\theta = \frac{B(T-T_i)}{T_i^2} \qquad (11)$$

The differential equation becomes

$$\frac{d\theta}{dx} = \frac{10000}{80} \frac{(-\Delta H)}{W} \frac{M A B}{C_p T_i^2 \ell} e^{-B/T_i} e^{\theta} \qquad (12)$$

Integrating across the entire filter and remembering that $\theta = 0$ when $T = T_i$ and $\int_0^\ell dx = \ell$ the following is obtained

$$1 - e^{-\theta\ell} = \frac{1000 (-\Delta H) M A B e^{-B/T_i}}{80 W C_p T_i^2} \qquad (13)$$

Where θ_ℓ is θ evaluated at ℓ, the exit end of the filter. It is clear that since $e^{-\theta\ell}$ approaches 0 as θ_ℓ (and the temperature) approaches infinity no steady state solutions are possible in which the quantity on the right is greater than one. It follows that the largest values of T_i for which a solution exists must satisfy the following equation

$$T_i^2 e^{B/T_i} = \frac{1000 (-\Delta H) M A B}{80 W C_p} \qquad (14)$$

The values of T_i obtained from this equation can be considered as the maximum inlet air temperature at which the heat generated by AN decomposition in the filter can be removed by the air. Higher temperatures will lead to thermal excrusions (uncontrolled temperature increases).

Values of T_i as a function of different assumed amounts of AN in the filter are shown in Table I. The following values were taken for the parameters in the equation.

$(- \Delta H)$ = 60,000 cal/mole
A = 4.4×10^9 sec^{-1}
B = 15000 °K^{-1}
W = 1630 g/sec (2900 cfm)
C_p = 0.24 cal/g °C

TABLE I

Maximum Air Inlet Temperature for Controlled Removal of Heat from Vessel Vent Filter by Forced Convection

M in Filter kg NH_4NO_3	Inlet Air Temperature, T_i	
	°K	°C
100	474	201
250	460	187
500	450	177
750	444	171
1000	439	169
2500	428	155

TABLE I CONT'D

M in Filter kg NH_4NO_3	Inlet Air Temperature, T_i	
	°K	°C
5000	419	146
7500	414	141
10000	410	137
20000	402	129
30000	398	125

Under normal operating conditions the temperature of the air to the vessel vent filter is only 50°C and the maximum value that has been used in the past is 80 - 85°C. These temperatures are considerably lower than those that would lead to thermal excursions even with the large quantities of AN present. Thirty thousand kg of AN would be nearly sufficient to fill the filter tank with solid material. The system should therefore, be safe against self-heating during normal operating conditions.

Loss of Air Flow

If the air flow to the filter were shut off, the only mechanism for heat transfer would be by conduction through the filter material (Fiberglas) to the walls of the filter and then to the canyon air by free convection. In the following discussion it will be assumed that the walls of the tank are at the same temperature as the canyon air (an assumption that will be justified later) and that the ammonium nitrate is uniformly distributed through the filter.

The self-heating problem was first discussed by Frank Kamenetsky[20], later by Rice[21], and finally more completely by Chambré'[22] whose development is given briefly below.

The steady state problem of heat conduction in a system where heat is continuously generated by chemical reaction is given by the equation

$$\lambda \nabla^2 T = -(-\Delta H)W \qquad (15)$$

where λ is the thermal conductivity $(-\Delta H)$ is the negative enthalpy of reaction and W is the reaction velocity. Combining this with the Arrhenius equation for reaction velocities the following is obtained

$$\nabla^2 T = - \frac{(-\Delta H)\ C\ A}{\lambda} e^{-B/T} \qquad (16)$$

Where C is the concentration of a reactant and A and B are parameters in the Arrhenius equation.

If it is again assumed that $\frac{T-T_0}{T}$ is small compared to one, (the same approximate can be made as the preceeding section) and if $\theta = \frac{B}{T_0^2}(T-T_0)$ (where T_0 is the temperature at the surface) it follows that

$$\nabla^2 \theta = - \left[\frac{(-\Delta H)\ B\ C\ A\ e^{-B/T_0}}{\lambda\ T_0^2} \right] e^\theta \qquad (17)$$

The above equation can be formulated for the case of a sphere or an infinitely long cylinder as follows

$$\frac{d^2\theta}{dZ^2} + \frac{K}{Z}\frac{d\theta}{dZ} = -\delta e^\theta \qquad (18)$$

Where $Z = X/\gamma$, where X is the space coordinate and γ is the significant geometric dimension (the radius of the sphere or the cylinder), K is 1 for a cylinder and 2 for a sphere, and

$$\delta = \frac{(-\Delta H)\ B\gamma^2 CA}{\lambda T_o^2}\ e^{-B/T_o} \qquad (19)$$

When the differential equations was solved with the appropriate boundary conditions

$$(\theta = 0 \text{ at } Z=1 \text{ and } \frac{d\theta}{dZ} = 0 \text{ at } Z=0)$$

it was found that solutions are possible only for values of $\delta \leq \delta$ where δcrit is a constant for each geometry. These values together with the corresponding maximum values of θ (ie θ (o))are shown below for the two geometries.

Cylinder	Sphere
δ crit = 2	δ crit = 3.32
θ max, crit = $\ell n4$ = 1.39	θ max, crit = 1.61

For values of δ larger than these the heat cannot be removed by conduction as fast as it is formed and the system will continue to heat up.

The actual problem we wish to solve is for the amount of ammonium nitrate that can be placed in a cylinder 4 ft in radius and 15 ft 7 inches long at various wall temperatures without exceeding a critical value that will cause it to continue to heat up. The calculations for the sphere and the infinite cylinder, both 4 ft in radius, bracket this problem, if the concentration of AN in each of them were the same as that in the finite cylinder. Heat losses from the sphere would be higher than for the finite cylinder, and will lead to values of the critical mass that are too large while heat losses for the infinite cylinder will lower them for the finite cylinder and will lead to critical masses that are too small.

Critical masses of ammonium nitrate were calculated for both the sphere and infinite cylinder from the definition of δ using concentrations calculated as follows:

$$C = \frac{M \times 1000}{80\ V} \qquad (20)$$

Where M is the number of kilograms of AN and V is the active volume of filter. Values of the parameters in the calculation are the following:

$(-\Delta H)$ = 60,000 cal/mole
γ = 121 cm (4 ft)
λ = 0.88 x 10^{-4} cal/cm.sec.^{o}C (thermal conductivity of glass wool)
A = 4.4 x 10^9 sec^{-1}
B = 15000 ^{o}C^{-1}
V = 1.30 x 10^7 cm^3
C = 0.96 x 10^{-6} M moles/cm3

Substituting these values into equation (19) yields

$$M = \frac{\gamma \delta T_o^2 \, e^{B/T_o}}{0.96 \times 10^{-6} \, (-\Delta H) \, \gamma^2 \, BA} \qquad (21)$$

$$M = 1.6 \times 10^{-21} \, \delta \, T_o^2 \, e^{\frac{15000}{T_o}} \qquad (22)$$

The results in Table II show that for any temperature likely to occur in the canyon buildings (30-40°C under ordinary conditions) self-heating cannot be a problem with the amounts of AN that can be contained in the filter, (22,000 kg is the maximum amount that could be present assuming an active volume of 1.3×10^7 cm^3 and a density of 1.7 g/cm^2).

TABLE II

Critical Mass of Ammonium Nitrate in the Vessel
Vent Filter for Various Surface Temperatures

Surface Temperature °C	Critical Mass M, kg of NH$_4$NO$_3$	
	Sphere δ = 3.32	Cylinder δ = 2.0
20	7.8×10^6	4.6×10^6
30	1.5×10^6	9.0×10^5
40	3.3×10^5	2.0×10^5
50	8.1×10^4	4.9×10^4
60	2.1×10^4	1.3×10^4
70	6100	3700
80	1900	1100
90	610	370
100	210	130
110	79	48
120	31	19
130	12	7

With the amounts of ammonium nitrate that are likely to be in the filter in the dry form (about 1000 kg) wall temperature in excess of 80°C would be required to lead to an excursion.

It was assumed for this calculation that the wall temperature would be about the same as the air temperature. This assumption can be justified as follows: The value of θ max, crit = 1.61 for a sphere can be used to calculate the maximum temperature (T max) in the center at the critical mass.

$$T_{max} = To + 1.61 \frac{To^2}{B} \qquad (23)$$

If it is now assumed that the temperature is uniform throughout the sphere at T_{max} and knowing M, the critical mass, a value can be calculated for the heat generation rate that is higher than the true value

$$Q = \frac{(-\Delta H) \, 1000 \, M \, A \, e^{-B/T_{max}}}{80} \qquad Cal/Sec$$

When this was done for To and M in Table II values of Q between 5.4 and 11.2 cal/sec were obtained. Heat transfer coefficients h for free convection in gases are generally in the range

1-4 BTU $ft^{-2}hr^{-1}{}_0F^{-1}$ or $(1.4 \times 10^{-4} - 5 \times 10^{-4}$ cal $cm^{-2}sec^{-1}{}_0C^{-1})^{23}$.

"h" is related to the heat generation rate Q and the surface area S by the following equation

$$Q = h S (To - T_\infty) \qquad (24)$$

Where $To - T_\infty$ is the difference between the wall temperature of the vessel and the air temperature at large distances. The surface area of the filter (sides and top only) is 4×10^5 cm^2 (440 ft^2). If the smallest value for the heat transfer coefficient (1.4×10^{-4}) and the largest value for the heat generation rate (11.2 cal/sec) are inserted into this equation

$$To - T_\infty = \frac{11.2}{1.4 \times 10^{-4} \times 4 \times 10^5} = 0.2^0C$$

Therefore, under the most adverse conditions the wall temperatures will only be a few tenths of a degree above the ambient air temperature.

Self-Heating Rate

Another consideration in the safety of the system is the length of time required for a thermal excursion to occur if air flow were shut off or the system became insulated in some other way, and the mass of AN exceeded the critical mass. In the following discussion it will be assumed that the system becomes completely adiabatic at a given initial temperature and that AN is the only material that absorbs heat. The rates of temperature increase calculated will therefore be maximum values because in a real system other materials will also absorb heat.

Considerations of heat balance lead to the following equation describing the rate of temperature increase.[24]

$$\frac{dT}{dt} = \frac{(-\Delta H) A e^{-B/T}}{C_v} \qquad (25)$$

Where T is the temperature in ^0K t, the time in seconds $(-\Delta H)$ the molar enthalpy of reaction, C_v the heat capacity of ammonium nitrate at constant volume and A and B are parameters of the Arrhenius equation.

Equation (25) can be solved but the form was not convenient to use. It was therefore solved numerically and the time necessary to go from the initial temperature To to 600^0K was determined. That final temperature was chosen because only about 0.25 seconds is required for the temperature to increase from 600^0K to 700^0K and the times get progressively shorter thereafter. The results of these calculations are shown in Table III. The quantities used in these calculations were:

$$(-\Delta H) = 60,000 \text{ cal/mole}$$
$$C_v = 38.5 \text{ cal/}^{\circ}C \text{ mole}$$
$$A = 1.58 \times 10^{13} \text{ hours}^{-1} \quad (4.4 \times 10^9 \text{ sec}^{-1})$$
$$B = 15000 \text{ }^{\circ}C^{-1}$$

TABLE III

Self-Heating Rate of Ammonium Nitrate

Initial Temperature °C	Time to Excursion Hours	
20	3.9×10^6	450 years
40	1.7×10^5	19 years
60	1.1×10^4	1.2 years
80	960	40 days
100	110	4.5 days
120	16	16 hours
140	2.7	2.7 hours
160	0.56	34 minutes
180	0.13	7.8 minutes
200	0.036	2.2 minutes
220	0.011	40 seconds

An approximate solution can be obtained for equation (25) by using the approximation described by equations (10) and (11). Equation (25) then becomes

$$\frac{d\theta}{dt} = \frac{(-\Delta H) \; B \; A \; e^{-B/T_o}}{C_v \; T_o^2} \; e^{\theta} \tag{26}$$

Where θ is defined by equation (11) and T_o is the initial temperature

Solution of equation (26) with the appropriate initial conditions ($\theta = 0$ when $t = 0$) yields

$$1 - e^{-\theta} = \frac{(-\Delta H) \; B \; A \; e^{-B/T_o}}{C_v \; T_o^2} \; t \tag{27}$$

When the temperature becomes infinite, θ also becomes infinite and $e^{-\theta}$ goes to zero. The time required for the temperature to become infinite is

$$t_{\infty} = \frac{C_v T_o^2 \; e^{B/T_o}}{(-\Delta H) \; B \; A} \tag{28}$$

or if t_{∞} is in hours

$$t_{\infty} = 2.7 \times 10^{-21} \; T_o^2 \; e^{+\frac{15000}{T_o}} \tag{29}$$

Table III shows that the minimum time required to heat the vessel vent filter to a dangerous level is quite large even at the highest initial temperature (80°C) likely to occur in it; at 80°C at least 40 days would be required. In an actual system much larger times would be necessary because materials other than AN will have to be heated and because of heat leaks to the outside.

Fires

Although a vessel vent filter containing reasonable amount of AN cannot spontaneously heat from canyon temperature to a dangerous level, heat from an external fire might produce serious consequences. There are no combustible materials in the canyon building in the vicinity of the filter and so an external fire in that area is very unlikely. The most serious is a fire elsewhere in the canyon from which heated gases are drawn into the vessel vent system and hence through the filter. The effects of three hypothetical fires will be considered to calculate this hazard: (1) A solvent fire in a tank (2) a solvent fire in a cell due to a ruptured tank, and (3) a fire in the vessel vent header itself.

Fire in a Solvent Tank

The amount of heat that can be generated per unit time by a solvent fire in a tank is limited by the availability of oxygen. The normal air sweep in a tank is 60 cfm (1700 liters.min), which corresponds to 68.4 g moles/min of air at $30^{\circ}C$ or 13.7 g moles of O_2/min. If the material burning is the normal paraffin hydrocarbon (principally n-dodecane) used as a diluent in the Purex solvent, the oxidation reaction is:

$$C_{12}H_{26} + 18.5\ O_2 \rightarrow 12\ CO_2 + 13\ H_2O$$
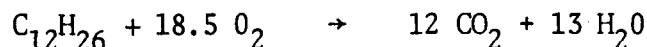
and the heat of combustion is[25] about 1800 KCal/mole of $C_{12}H_{26}$. The heat generated per mole of O_2 consumed is therefore 97 KCal/mole O_2 and the maximum heat generated rate, q, is

$$q = 97\ \text{KCal/mole } O_2 \times 13.7\ \text{mole/min} \approx 1300\ \text{KCal/min}$$

If the hot gases from the burning tank are mixed with the air (Cp = 0.24) in the vessel vent header flowing at 2900 cfm or 96 Kg/min and no heat is lost to the surroundings the temperature increase will be

$$\Delta T^{\circ}C = \frac{q}{CpW} = \frac{1300}{0.24 \times 96} = 56^{\circ}C$$

Even if the original air temperature were $50^{\circ}C$ (the maximum air temperature in the H-Area hot canyon system) this would only lead to an air inlet temperature to the filter of $106^{\circ}C$ which should not lead to an uncontrolled excursion (see Table I).

Fire in Cell (Ruptured Solvent Tank)

If solvent should spill into the bottom of a cell in a canyon due to the rupture of a tank, and then ignite, heat from the fire could be drawn into the vessel vent system through four different vessels in the cell. This would introduce more heat than a fire in a single tank. The effect of such a fire on the temperature of the air entering the vessel vent filter was estimated as follows:

The adiabatic (maximum) flame temperature for hydrocarbons burning in air is[26] about $4000^{\circ}F$ or $2200^{\circ}C$. If the mass flow of air W_H, from each vessel into the header is assumed to be independent of temperature (i.e., 2 Kg/min) as well as the heat capacity of air, heat balance considerations lead to the following equation

$$T_f = \frac{T_H \eta W_H + T_c W_c}{W_c + \eta W_H} \qquad (31)$$

where T_f, T_H and T_c are the temperatures of the air entering the filter, the hot gases from the fire, and the cold air being drawn into the other tanks respectively. W_c is the total mass flow of air into the header from tanks not involved in the fire and n is the number of tanks involved in the fire.

T_f was calculated to be 210°C with the assumption that T_H = 2200°C, T_c = 30°C, W_H = 2 Kg/min, n = 4, and the total mass flow $W_c + \eta W_H$ = 96 Kg/min. The calculated inlet temperature to the filter is sufficiently high to cause spontaneous heating of the filter with as little as 100 Kg of ammonium nitrate present.

The assumption that the mass flow rate is independent of the temperature probably over-estimates the effect of such a fire. Another way of approaching the problem is as follows: The flow of a fluid through a circular pipe can be described by the equation[27]

$$f \rho V^2 = K \qquad (32)$$

Where f is the Fanning friction factor, ρ the density and V the linear velocity. K is a function of the length and diameter of the pipe and the pressure drop across it but will be constant when these are constant. The Reynolds number for 60 cfm air through a 3" pipe (diameter of exhaust from a tank to the vessel vent header) is 1.3×10^6 at 30°C. In this region the friction factor is nearly independent of Reynolds number and to a first approximation can be assumed to be constant. With this assumption it can be shown that

$$\frac{W_1}{W_2} = \frac{\rho_1 V_1}{\rho_2 V_2} = \sqrt{\frac{\rho_1}{\rho_2}} = \sqrt{\frac{T_2}{T_1}} \qquad (33)$$

Where W_1 and W_2 are the mass flows of air at temperatures T_1 and T_2.

The flow of air at 2200°C into an inlet where the flow at 30°C was about 2.0 Kg/min, is

$$W_H = 2 \times \frac{303}{2473} = 0.70 \text{ Kg/min}$$

with this value of W_H and the assumptions made previously, T_f was found to be 93°C. That temperature should not lead to spontaneous heating of a filter (Table I).

The second calculation of the temperature of the inlet air to the filter is probably a closer approximation than the first, but the assumptions are uncertain enough that it is not possible to state categorically that the system would be safe in the event of such solvent fire.

Fire in the Vessel Vent Header

A fire in the vessel vent header would be of concern if it involved sufficient fuel to generate significant heat. Examination of the header in the H-Area hot canyon showed that the only foreign matter present was a layer of black granular solid about three inches wide and 1/16 inch deep. The material was analyzed[28] to be primarily corrosion products of stainless steel together with small amounts of ammonium nitrate. It was estimated that the header contained no more than 7.2 Kg of NH_4NO_3.

If ammonium nitrate in the header were to ignite, the most rapid burning that could occur is fume-off burning, in which the burning rate is controlled by the rate of thermal decomposition at the fume-off temperature (290°C at 1 atmosphere pressure). The first order rate constant at that temperature is[18] about 0.002 sec^{-1} or 0.12 min^{-1}. The burning rate would then be 0.86 Kg/min and the heat generation rate, assuming $-\Delta H = 60$ KCal/mole, would be 650 KCal/min. This would increase the temperature of the air flow-into the filter about 28°C if no heat were lost to the walls. If the initial air temperature were 30°C, the maximum temperature of air entering the filter would only be 58°C, which would not lead to spontaneous heating. Furthermore the reaction would die out rapidly because the half life of ammonium nitrate at the fume off temperature is only about six minutes.

CONSEQUENCES OF AN EXPLOSION

If a fire or uncontrolled self-heating should occur in the vessel vent filter it might develop into a detonation. In the following assessment of the consequences of an explosion we assume the worst possible case: that the ammonium nitrate in the filter contains enough fuel to make a balanced explosive and that it has detonated. Two consequences of a detonation were identified (1) structural damage to the canyon building and its equipment by the shock wave and (2) pressurization of the canyon building by gas generated by the explosion, producing a reversal of air flow and the spread of radio-active contamination outside the canyons.

Structural Damage

An analysis of the structural damage that would be done by the detonation of 600 Kg of ammonium nitrate in a vessel vent filter was performed by W. W. F. Yau and has been reported in detail in a separate report[2]. The extent of structural damage can be summarized as follows:

1) Cracking and possible partial collapse of the inner canyon walls
2) Movement, collisions and fracture of process tanks
3) Fragmentation of the fire curtains
4) The cell cover could be propelled to the level of the overhead crane.

Pressurization of a Canyon

If a charge of ammonium nitrate were to detonate in the canyon, the hot gases from the explosion would rapidly expand and adiabatically compress the air in the canyon. The resulting pressure increase would cause air to flow from the canyon through air supply ducts and spread contamination to normally clean areas. The pressure increase can be estimated as follows; assuming the canyon walls are intact:

Let V_g be the volume of gas generated by the explosion after it has adiabatically expanded to atmospheric pressure and V be the volume of the canyon, which contains air initially at atmospheric pressure. If each of these volumes were then adiabatically compressed so that the sums of their volumes were equal to the volume of the canyon and the pressure in each were the same, the pressure conditions inside the canyon immediately after the detonation and expansion of the hot explosion gases should be obtained. If it is further assumed that the heat capacity ratio, $\gamma = Cp/Cv$ for the explosion gas and air are the same, the pressure P in atmospheres after the explosion will be

$$P = \left(\frac{V + V_g}{V} \right)^{\gamma} \qquad (34)$$

and the pressure increase, ΔP_o, in inches of water will be

$$\Delta P_o = 407 \left[\left(\frac{V + V_g}{V} \right)^\gamma - 1 \right] \qquad (35)$$

The volume of the canyon was estimated to be 5.1×10^7 l; V_g was obtained from data furnished by F. A. Loving and is given by the equation $V_g = 1.16 \times 10^3$ M liters, where M is the number of kilograms of AN involved in the explosion: γ for air is 1.4. Then

$$\Delta P_o = 407 \left[(1 + 2.27 \times 10^{-5} M)^{1.4} - 1 \right] \qquad (36)$$

TABLE IV

Pressurization of Canyon by Gas Generaged in Explosion

Kg of NH_4NO_3	V_g liters	ΔP_o inches of H_2O	Time to recover seconds
100	1.16×10^5	1.29	3.4
500	5.78×10^5	6.48	7.0
1000	1.16×10^6	13.0	8.8
5000	5.78×10^6	66.1	13.0
10000	1.16×10^7	135.	14.9

Table IV summarizes the results of calculations of the pressure increase in the canyon due to the explosion of various amounts of ammonium nitrate. The canyons normally operate at a pressure of -0.5 inches of water so that the gas generated by the explosion of as little as 100 Kg of AN should be enough to cause a significant reversal of air flow. The column at the extreme right is the estimated time necessary for the excess pressure in the canyon to drop to zero.

Times to recover from a pressure surge were obtained from the equation

$$\ln \frac{(\Delta P + \Delta Pn)}{(\Delta Po + \Delta Pn)} = - Bt \qquad (38)$$

Where ΔP is the pressure difference between the canyon and the outside at time, t, ΔPo is the value of ΔP immediately after the expansion of the explosive, ΔPn is the negative of ΔP under normal operating conditions. and

$$B = \frac{Pn}{\Delta Pn} \frac{\dot{U}}{V} \ sec^{-1} \qquad (39)$$

Where Pn is the absolute pressure of canyon air under normal operating conditions, U is flow of canyon air in liters per socond under normal operating conditions and V is the volume of the canyon in liters.

Equation (38) was derived under the assumption that air flows from the canyon through the exhaust tunnel at a constant rate but at a rate proportional to the pressure difference, ΔP, through the supply tunnel. The rate constant, B, for the process was established from our knowledge of the flow into the canyon (50,000 cfm) under a known head (-0,5 inches of water). B was found to be 0.376 sec^{-1}. The recovery times were found by solving equation (38) for t with $\Delta P = 0$, $\Delta Pn = 0.5$ and with ΔPo equal to the values shown on Table IV.

## SOURCES OF AMMONIUM NITRATE IN THE VESSEL VENT SYSTEM

The origin of ammonium nitrate in the vessel vent system was traced by Separations Technology to the neutralization of waste concentrates. When acidic waste containing ammonium ion is neutralized some of the ammonia formed is volatilized and transported by the air sweep through the tank into the vessel vent header where it reacts with nitric acid fumes from other tanks to form AN. The AN particles are then collected by the vessel vent filter.

The ammonium ions in the waste concentrate streams originate from two sources (1) impurities in the process chemicals and (2) reactions of nitrogen-containing chemicals such as sulfamic acid and hydrazine during chemical processing. The amounts of ammonium nitrate introduced as impurities in essential materials has been determined to be $\sim$ 9 Kg per evaporator batch by Works Technical. Most of the ammonium ion in waste (>90%) comes from reactions of process chemicals. The following discussion considers reactions by which ammonium ion is formed from sulfamic acid, hydrazine, and hydroxylamine, according to the published literature, as well as reactions that will destroy these substances.

Sulfamic Acid

There are two reactions of sulfamic acid of interest for the present problem: hydrolysis and reaction with nitrous acid.

The kinetics of the hydrolysis reaction

$$NH_2SO_2OH + H_2O \rightarrow NH_4HSO_4 \qquad (40)$$
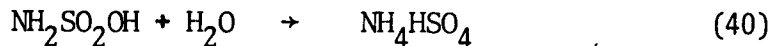
has been studies by several investigators[31-35] under a wide variety of conditions of temperature, acidity and ionic strength. The consensus of more recent investigations is that the rate is proportional to the concentration of undissociated sulfamic acid

$$\frac{dS_t}{dt} = -k(HS) \qquad (41)$$

where S_t is the concentration of sulfamic acid plus sulfamate ion, (HS) is that of free sulfamic acid alone, and k is the first order rate constant in hours^{-1}. The concentration of free sulfamic acid (HS) can be written in terms of (S_t) and the acid dissociation constant, K_c for the reaction.

$$HS \rightarrow S^- + H^+ \qquad (42)$$

so that the first order rate equation for the hydrolysis of total sulfamate is

$$\frac{dS_t}{dt} = - \frac{k}{[1 + K_c/(H^+)]} S_t = k'S_t \qquad (43)$$

Both k and K_c are functions of temperature while K_c is also a function of ionic strength, μ. The rate data of the various authors can be represented accurately over the entire range of temperature and ionic strength by properly accounting for these effects on K_c. For estimating hydrolysis rates in process solutions where the ionic strength and acidity are usually quite high (μ and $H^+ \geqslant 1$), and great accuracy is not required, K_c can be assumed constant.

The following equations were found to fit the published data reasonably well (± 10%):

$$\ln K = 41.260 - 15250/T \qquad (44)$$

$$K' = \frac{K}{(1 + .36/(H^+))} \qquad (45)$$

Where T is the temperature in $^\circ K$, k and k' are rate constants in hours^{-1} and (H$^+$) is the acid concentration in moles/liter.

Experimental data have only been reported up to temperature of 98°C. However, equations (44) and (45) have been used to extrapolate to the boiling point of 8M HNO$_3$ (110-115°C).

The first order rate constants for sulfamic acid hydrolysis in 8M acid as a function of temperature are shown together with the corresponding half lives of sulfamic acid in Table V.

TABLE V

Hydrolysis Rates of Sulfamic Acid in 8M HNO$_3$ at Various Temperature

T $^\circ$C	K', hours^{-1}	t 1/2 hours
30	0.000110	6300
40	0.000550	1300
50	0.00248	280
60	0.0103	67
70	0.0390	18
80	0.137	5.0
90	0.452	1.5
100	1.39	0.50
110	4.05	0.17
115	6.77	0.10

The rate constants show that sulfamic acid will be hydrolyzed only slightly during chemical processing because the highest temperature reached is 55°C and then only for a half hour. Under those conditions less than half a per cent of the sulfamic acid should hydrolyze. In a waste evaporator where the temperature exceeds 110°C, the half life is only a few minutes and virtually all remaining sulfamic acid should hydrolyze.

The kinetics of the reaction between nitrous and sulfamic acid

$$HNO_2 + H_2NSO_3H \rightarrow N_2 + H_2O + H_2SO_4 \qquad (46)$$

have been studied in acetate[36], perchlorate[37] and nitrate media.[38] These three studies agreed qualitatively in that the rate is given by the equation

$$\text{Rate} = K \, (H^+) \, (HNO_2) \, (H_2NSO_3^-) \qquad (47)$$

and the quantitative agreement among the studies is quite good. Li and Ritter[36] give the following equation to describe the rate as a function of the temperature T in $^\circ$C and the ionic strength μ. The rate constant k is in $(\ell/\text{mole})^2$ min^{-2}.

$$\log_{10}K = 5.027 + (T-25)/31.2 - 0.72 \sqrt{\mu}/(1 + \sqrt{\mu}) \quad (48)$$

Biddle and Miles[38] report spectroscopic evidence for the existence of an intermediate product of nitrous and sulfamic acids that has only transient existence. The spectral band corresponding to the intermediate reaches a maximum absorbance after about 30 milliseconds in a solution of 0.01M HNO_2 and 0.05M H_2NSO_3H and then decays.

The rate constants under process conditions are sufficiently high that sulfamic acid should not persist for long in the presence of excess nitrous acid. At 25°C and 1M HNO_3 the second order rate constant is about 10^4 min^{-1} (mole/liter)$^{-1}$. If there is an excess of 10% nitrous acid over that needed to react with the sulfamic acid whose initial concentration is given by S_0 the time required to remove 99% of the sulfamic acid is shown in the following table.

| So Initial Sulfamic Acid Concentration moles/liter	Time in Minutes to Remove 99% of Sulfamic Acid
0.001	2.3
0.01	0.23
0.05	0.046
0.1	0.023

Hydrazine

The chemistry of hydrazine in aqueous solutions has been reviewed by Yost and Russell[39] and by Audrieth and Ogg[40].

Hydrazine in aqueous solution can act as either an oxidizing or a reducing agent. With powerful reducing agents such as Zn, Sn, Sn^{2+} and Ti^{3+} reduction of hydrazine to ammonia is observed. With oxidizing agents one or several products may result including N_2, NH_4^+ and HN_3 (hydrazoic acid).

One-electron exidizing agents, such as Fe^{3+}, Mn^{3+}, and Ni^{3+}, react with hydrazine to product ammonia and nitrogen but no HN_3, as in the following:

$$N_2H_5^+ + Fe^{3+} \rightarrow NH_4^+ + 1/2\, N_2 + H^+ + Fe^{2+} \quad (49)$$
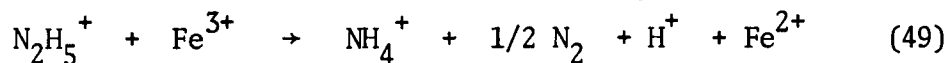
Two electron oxidizing agents such as peroxy disulfate, hydrogen peroxide, and chlorate react to some extent by the mechanism

$$2N_2H_5^+ \rightarrow HN_3 + NH_4^+ + 5H^+ + 4e \quad (50)$$
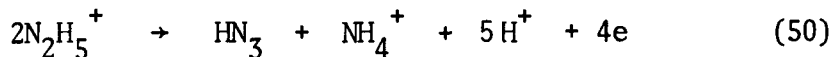
but may also proceed along a path to give nitrogen or ammonia.

Polyelectron oxidizing agents may act as one- or two- electron oxidizing agents, or as a mixture of both. In only a few instances, as with the reaction of hydrazine with the halogens, is the product simply nitrogen

$$N_2H_5^+ + 2\, Br_2 \rightarrow N_2 + 5H^+ + 4Br^- \quad (51)$$
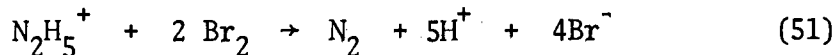
Hydrazine in acidic media spontaneously decomposes in the presence of a platinum catalyst according to the following equation:

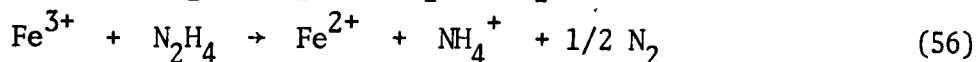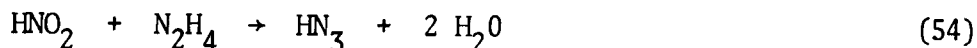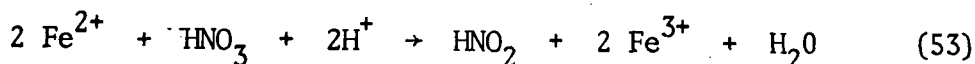$$3\ N_2H_5^+ + H^+ \rightarrow N_2 + 4\ NH_4^+ \tag{52}$$
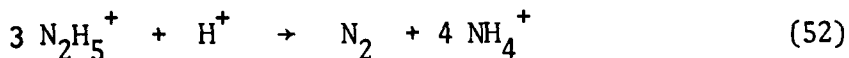
in alkaline media some hydrogen gas may be produced as well.

Hydrazine is stable toward oxidation by atmospheric oxygen in acidic media but oxidizes in alkaline solutions fairly rapidly. Ammonia has been reported as a product of that reaction.

References to the reaction between nitric acid and hydrazine have been found in the older literature but the products of the reaction were not reported. The direct reaction is slow at room temperature but boiling concentrated nitric acid as in an evaporator will react and might produce some ammonia.

In plant process solutions containing iron, hydrazine, and nitric acid the following reactions have been shown to occur during the heat kill in the frames process.[41]

$$2\ Fe^{2+} + HNO_3 + 2H^+ \rightarrow HNO_2 + 2\ Fe^{3+} + H_2O \tag{53}$$

$$HNO_2 + N_2H_4 \rightarrow HN_3 + 2\ H_2O \tag{54}$$

$$HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O \tag{55}$$

$$Fe^{3+} + N_2H_4 \rightarrow Fe^{2+} + NH_4^+ + 1/2\ N_2 \tag{56}$$

The sum of these reactions is equivalent to a catalytic oxidation of hydrazine by nitric acid:

$$2\ HNO_3 + 5\ N_2H_4 + 4H^+ \rightarrow N_2O + 3N_2 + 4\ NH_4^+ + 5\ H_2O \tag{57}$$
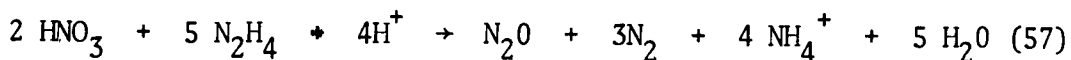
in which four moles of ammonium ion are produced for five moles of hydrazine consumed.

Of special interest in process chemistry is also the reaction between hydrazine and nitrous acid represented by equations (54) and (55). The overall reaction can be written.

$$N_2H_4 + 2HNO_2 \rightarrow N_2O + N_2 + 3\ H_2O \tag{58}$$
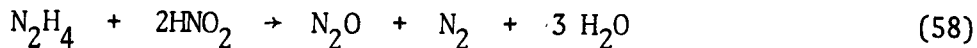
and presents a way by which hydrazine can be destroyed to produce innocuous products and no ammonia. The kinetics of the first step in this reaction (reaction 54) has been studied by Biddle and Miles.[38] The rate of reaction in 2M HNO$_3$ is 5-10 times faster than that between nitrous and sulfamic acid and increases quadratically with increasing acidity. Hydrazine should therefore only persist for a few minutes at the most in the presence of excess nitrous acid. The hydrazoic acid which forms as a product of this reaction also reacts rapidly with nitrous acid.[41]

Hydroxylamine

The chemistry of hydroxylamine in process solutions has been discussed by McKibben and Bercaw[42]. Hydroxylamine reacts with oxidizing agents such as ferric ion according to the following reaction

$$2 \; NH_2OH \; + \; 4 \; Fe^{3+} \; \rightarrow \; 4 \; Fe^{2+} \; + \; N_2O \; + \; H_2O \; + \; 4 \; H^+ \qquad (59)$$
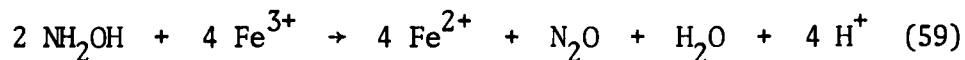
Dilute nitric acid solutions are stable but stronger acid solutions are increasingly unstable, especially at elevated temperatures. In a solution originally containing 0.8M hydroxylamine nitrate and 1.0 M nitric acid all of the hydroxylamine was destroyed upon boiling for one half hour according to the reaction

$$4 \; NH_2OH \; + \; 2 \; HNO_3 \; \rightarrow \; 3 \; N_2O \; + \; 7 \; H_2O \qquad (60)$$
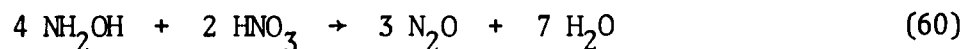
Alkaline solutions of hydroxylamine nitrate are unstable and decompose according to the reactions

$$4 \; H_2NOH \cdot HNO_3 \qquad + \; 4 \; OH^- \; \rightarrow \; N_2O \; + \; 2NH_3 \; + \; 4 \; NO_3^- \; + \; 7H_2O \qquad (61)$$
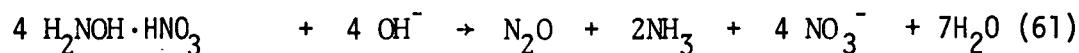
It therefore appears that hydroxylamine could also produce ammonia if it were present in alkaline waste solution. However, it is unlikely that any hydroxylamine could survive acidic evaporation. It is therefore not a likely source of ammonia in waste streams.

The kinetics of the reaction between hydroxylamine and nitrous acid (Reaction 82) have been studied by Hughes and Stedman.[43]

$$HNO_2 \; + \; NH_2OH \; \rightarrow \; N_2O \; + \; 2H_2O \qquad (62)$$
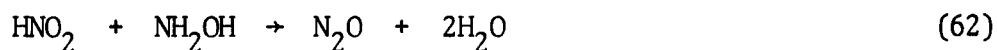
The rate equation for the reaction in perchloric acid is

$$Rate \; = \; K_3(H^+) \; (HNO_2) \; (NH_3OH^+) \qquad (63)$$

and the rate constant, k_3, is about 0.24 (mole^{-2} liters^2 sec^{-2}) at 0°C with H$^+$ 0.025M. This rate is slower than the rates of the corresponding reaction with hydrazine and sulfamic acid by a factor of about 50 and so nitrous acid will react with sulfamic acid and hydrazine in preference to hydroxylamine if all three are present in comparable amounts.

POSSIBLE WAYS TO REDUCE NH$_4$NO$_3$ ACCUMULATION

There are a number of possible actions to suppress or reduce the rate of AN accumulation in the vessel vent filter:

1) Destruction of ammonia precursors.
2) Destruction of ammonium before waste is neutralized.
3) Suppression of ammonia volatilization.
4) Removal of NH$_3$ from the air stream before it enters the header.
5) Periodic removal of NH$_4$NO$_3$ from the filter.

Destruction of Precursors

The destruction of both sulfamic acid and hydrazine with excess nitrous acid will proceed rapidly at ambient temperature. This will not affect, however, the ammonia occurring as impurities in the reagents, in evaporator overheads returning from the waste tank farm nor that produced from the percursors during chemical processing.

Destruction of the precursors with nitrous acid is now being practiced in H-Area and appears effective in reducing the amount of ammonia released into the vessel vent system.

## Destruction of Ammonium Ion Before Neutralization

Ammonium ion is a reducing agent and might be destroyed by oxidation if a suitable oxidizing agent that is compatible with the rest of the system (i.e., will not volatilize Ru or corrode the tanks, etc.) could be found. Nitrous acid appears promising for this purpose.

The reaction between ammonium ion and nitrous acid has been studied by Able, et. al.,[44] and by Dusenbury and Powell.[45] The later work showed that the reaction

$$NH_4^+ + HNO_2 \rightarrow N_2 + 2H_2O + H^+ \qquad (64)$$
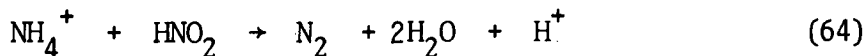
proceeded at a rate proportional to the product of the ammonium ion and nitrous acid concentrations. Their rate data suggested that at elevated temperature and in the presence of sufficient nitrous acid the reaction should oxidize most of the ammonium ion within an hour.

In the laboratory test nitric oxide gas was bubbled into nitric acid solutions containing ammonium ion at temperatures between $70^\circ C$ and $100^\circ C$. Nitric oxide addition produced nitrous acid according to the reaction:

$$2 \, NO + HNO_3 + H_2O \rightleftarrows 3 \, HNO_2 \qquad (65)$$
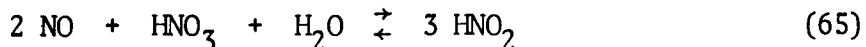
Since NO is a gas the concentration of nitrous acid will be the maximum that can exist at equilibrium under atmospheric pressure. First order rate constants as high as 6 hr^{-1} for ammonium ion destruction were obtained in 8M nitric acid at 90 - 100°C. These rates correspond to a half-life for ammonia ion of about 7 minutes, or the destruction of 99.8% of the ammonia within one hour. Other tests showed that destruction of ammonia can also be accomplished by adding $Na NO_2$ to form nitrous acid.

The advantages of this treatment are that it introduces no unfamiliar process chemicals, does not add to waste solids, and destroys all ammonium ion. The disadvantages are the time required and the problems of implementing it in the plant.

Suppression of Ammonia Volatilization after Neutralization

Most of the ammonia enters the vessel vent systems via the 60 cfm air sweep over the ammonia bearing solutions in the tank after neutralization of the waste. If the air sweep were cut off or the tank were disconnected from the vessel vent system during and after neutralization, the introduction of ammonium nitrate into the vessel vent system would be reduced. The problem would not be eliminated entirely however because some ammonia would get into the vent system when waste was transferred to the tank farm. Disconnecting the neutralization tank from the vent system would allow some ammonia to enter the canyon itself; although the amount would be small, it is uncertain where it would end up.
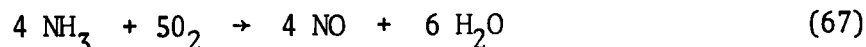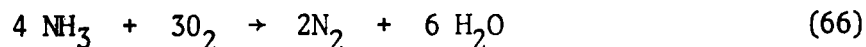
Another approach to the problem is to add something to the waste that will react with the ammonia to produce a nonvolatile product. One such reaction is that of formaldehyde with ammonia to produce hexamethylenetetramine.[46]

$$6 \ HCHO \ + \ 4 \ NH_3 \ \rightarrow \ (CH_2)_6N_4 \ + \ 6 \ H_2O \qquad\qquad (65)$$
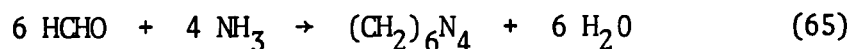
Preliminary tests at SRL indicate that this reaction is effective in reducing ammonia volatilization. The advantage of the method is that it requires the addition only of one reagent with no additional processing time required. The disadvantage is that little is known about reactions that the product might undergo in the waste tanks.

Removal of NH_3 from the Air Stream Before Reaching the Header

Ammonia could probably be removed from the air stream after it has volatilized by air oxidation according to one of the following equations:

$$4 \ NH_3 \ + \ 3O_2 \ \rightarrow \ 2N_2 \ + \ 6 \ H_2O \qquad\qquad (66)$$

$$4 \ NH_3 \ + \ 5O_2 \ \rightarrow \ 4 \ NO \ + \ 6 \ H_2O \qquad\qquad (67)$$

Both of these reactions are catalyzed by platinum and by heavy metal oxides. The gas pahse oxidation would probably require heating the air stream from the neutralizer tank to 500-700°C and passing it through the catalyst.

The advantage of this procedure are that no additional processing time is involved and the products of the reaction are innocuous. The disadvantages are that considerable development work will be required to design and oxidizer unit compatible with plant equipment and considerable capital expense will be required to build and install it.

Periodic Removal of AN from Filter

Removal of ammonium nitrate from the filters by flushing with water is the primary procedure that has been utilized to reduce the hazard of ammonium nitrate accumulation. The method is straightforward, and effectively removes AN, but there are certain disadvantages. The plant must be shut down for several days to allow the draining and flushing of the present filters.

Flushing the high efficiency "Fiberglas" filter now used in H-Area hot canyon will decrease its efficiency; installation of new high efficiency filters designed for flushing is now under study; these would be expensive. A further difficulty with the concept of flushing the filters is that large amounts of ammonium nitrate solutions are generated and must be disposed of. If these solutions are neutralized with caustic and transferred to the tank farm, much of the ammonia will immediately be returned to the vessel vent system from the neutralization tank, and the remainder will be transferred to the waste tanks. From the waste tanks most of the ammonia will volatilize into the overheads of the tank farm evaporators and may be returned to the canyon if this water is returned for use in processing.

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